

James F. Wishart

Department of Chemistry
Brookhaven National Laboratory
Upton, NY 11973
(631) 344-4327 Fax (631) 344-5815

E-mail: wishart@bnl.gov

Home Address:
190 Maple Road
Wading River, NY 11792
(631) 929-4407

Positions Held

Chemist

Department of Chemistry, Brookhaven National Laboratory, Upton, New York
September, 1987 to present

Assistant Chemist, 1987-1989. Associate Chemist, 1989-1992. Co-Principal Investigator in the Photochemistry and Radiation Chemistry Group. Construction Project Manager and Facility Supervisor of the Laser-Electron Accelerator Facility (LEAF). Research interests include radiation chemistry and reactions in ionic liquids, long-distance electron transfer, energy and electron transfer in dendrimers, studies of electron transfer and substitution mechanisms using high-pressure techniques, the reactivity of energetic inorganic species, and the development of new accelerators and new detection techniques in pulse radiolysis.

Co-editor, "Photochemistry and Radiation Chemistry: Complementary Methods for the Study of Electron Transfer", *Advances in Chemistry Series*, vol. 254. Organizer, Tutorial on Radiation Chemistry Principles and Applications, 209th ACS National Meeting, Inorganic Division, Anaheim, CA, April 2, 1995. Co-organizer, Symposium on Complementarity of Photochemistry and Radiation Chemistry in the Study of Electron Transfer, 209th ACS National Meeting, Inorganic Division, Anaheim, CA, April 2-5, 1995.

Postdoctoral Research Fellow

Department of Chemistry, Rutgers, the State University of New Jersey, New Brunswick, NJ
January, 1985 to August, 1987

In association with Prof. Stephan Isied. Constructed an excimer and dye laser flash photolysis system with cryostat and Macintosh-based control and data analysis system. Investigated long distance electron transfer in cytochrome c using covalently-linked ruthenium polypyridine complexes, and the rates of electron transfer across rigid oligopeptide bridges as a function of distance. Conducted enthalpy measurements on the binding of platinum and ruthenium complexes to nucleotides with Prof. Kenneth Breslauer.

Education

Doctor of Philosophy in Inorganic Chemistry

Stanford University, Stanford, California
September, 1979 to January, 1985

Research advisor: Professor Henry Taube.

National Science Foundation Graduate Fellow, 1980-83.

Dissertation title: *Thermodynamics of Mononuclear and Binuclear Ruthenium Ammine Complexes*.

Research topics included substitution and redox thermodynamics of ruthenium complexes, the nature of certain mixed-valence binuclear complexes, and quantitative approaches to back-bonding in ruthenium(II) and osmium(II) compounds. Work involved platinum-group synthesis, electrochemistry, batch, flow, titration and solution calorimetry, substitution and electron transfer kinetics, X-ray crystallography, and computerized data acquisition and analysis. Member, University Graduate Housing and Chemistry Department Safety Committees. Supervised two undergraduate research associates.

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Bachelor of Science in Chemistry

Massachusetts Institute of Technology, Cambridge, Massachusetts
September, 1976 to June, 1979

Supplemented the standard curriculum with graduate courses in molecular spectroscopy, advanced inorganic chemistry, and organometallic chemistry. Humanities concentration was Art. Served as vice president and treasurer of dormitory and on New Undergraduate Housing Committee. Undergraduate research was done at Wayne State University in my hometown of Detroit, with Prof. Richard Lintvedt during the summers of 1978 and 1979.

Teaching Experience

Stanford University: Teaching Assistant, first quarter Inorganic Chemistry, for Keith Hodgson, Winter 1984 (Gave a ninety-minute lecture on substitution and electron transfer mechanisms). Lecturer and TA, second quarter Inorganic Chemistry, with Henry Taube and Keith Woo, Spring 1982 (Gave nine lectures (1/3 of the course) on ligand field theory, molecular orbital theory, transition metal spectroscopy, and magnetism. Shared administrative responsibility for the course). TA, first quarter Inorganic Chemistry, for Keith Hodgson, Winter 1982. TA, second quarter Inorganic Chemistry, for Henry Taube, Spring 1981. Head Teaching Assistant, second quarter Organic Chemistry for K. Barry Sharpless, Spring 1980 (Prepared demonstrations, collaborated in test preparation and final grading). TA, Analytical Laboratory, for Keith Hodgson, Winter 1980. TA, General Chemistry, for Hans C. Andersen, Fall 1979.

Other Experience

Research Assistant, Wayne State University, Detroit, MI, June to September, 1978 and 1979.
Studied dicopperbistriketonates and related molecules with Prof. Richard Lintvedt. Performed original organic and inorganic synthesis and non-aqueous electrochemistry. Synthesized a new triketone which led to an interesting series of complexes.

Additional Information

Born July 21, 1958 in Detroit, Michigan. Member, American Chemical Society (Inorganic and Physical Divisions), American Association for the Advancement of Science, and Miller Trust for Radiation Chemistry.

References

Dr. John Miller, BNL; Dr. Richard Holroyd, BNL (retired); Dr. Norman Sutin, BNL (retired); Dr. Harold Schwarz, BNL (retired); Prof. Stephan Isied, Rutgers University; Prof. Henry Taube, Stanford University (emeritus).

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List of Publications

- Synthesis, Structure, and Magnetism of a New Type of π -Molecular Complex Containing Binuclear Copper(II) Complexes and Benzene: Bis[2,2-dimethyl-7-(phenylimino)-3,5,7-octanetrionato]dicopper(II)-Benzene and Bis[2,2-dimethyl-7-((4-nitrophenyl)imino)-3,5,7-octanetrionato]dicopper(II)-Bis(benzene)*
J. F. Wishart, C. Ceccarelli, R. L. Lintvedt, J. M. Berg, D. P. Foley, T. Frey, J. E. Hahn, K. O. Hodgson and R. Weis *Inorg. Chem.* **22**, 1667-1671 (1983)
- Enthalpies of Reaction of Pentaammineruthenium(II) Complexes*
J. F. Wishart, H. Taube, K. J. Breslauer and S. S. Isied *Inorg. Chem.* **23**, 2997-3001 (1984)
- Backbonding Effects of Osmium(III): The Crystal Structure of μ -Pyrazinedecaamminediosmium(II) Chloride Dihydrate*
A. Bino, P. A. Lay, H. Taube and J. F. Wishart *Inorg. Chem.* **24**, 3969-3971 (1985)
- The Enthalpy of Formation of Nitrosylpentaammineruthenium(II) from $NO^{+}_{(aq)}$ and Aquopentaammineruthenium(II)*
J. F. Wishart, H. Taube, K. J. Breslauer and S. S. Isied *Inorg. Chem.* **25**, 1479-1481 (1986)
- A Very Short Ruthenium(II) - Nitrogen Heterocycle Bond: The Crystal Structures of Pentaammine(N-methylpyrazinium)ruthenium(II) Iodide and Pentaammine(N-methylpyrazinium)ruthenium(III) p-Toluenesulfonate Pentahydrate*
J. F. Wishart, A. Bino and H. Taube *Inorg. Chem.* **25**, 3318-3321 (1986)
- The Distance Dependence of Intramolecular Electron-Transfer Rates: Importance of the Nuclear Factor*
S. S. Isied, A. Vassilian, J. F. Wishart, C. Creutz, H. A. Schwarz and N. Sutin
J. Am. Chem. Soc. **110**, 635-637 (1988)
- A Dissociative Pathway for Equilibration of a Hydrido $CoL(H)^{2+}$ Complex with CO_2 and CO : Ligand Binding Constants in the Macroyclic [14]Dienecobalt(I) System*
C. Creutz, H. A. Schwarz, J. F. Wishart, E. Fujita and N. Sutin *J. Am. Chem. Soc.* **111**, 1153-1154 (1989)
- Arene-to-Alkyne Linkage Isomerizations of Diphenylacetylene on Pentaammineosmium*
W. D. Harman, J. F. Wishart and H. Taube *Inorg. Chem.* **28**, 2411-2413 (1989)
- Report of the Workshop on the Proposed Pulse Radiolysis Facility at Brookhaven National Laboratory*
C. Creutz, H. A. Schwarz and J. F. Wishart BNL Report, BNL-52229, (1989)
- Electron Transfer Across Polypeptides. 6. Long Range Electron Transfer in Osmium-Ruthenium Binuclear Complexes Bridged with Oligoproline Peptides*
A. Vassilian, J. F. Wishart, B. van Hemelryck, H. Schwarz and S. S. Isied
J. Am. Chem. Soc. **112**, 7278-7286 (1990)
- Thermodynamics and Kinetics of Carbon Dioxide Binding to Two Stereoisomers of a Cobalt(I) Macrocycle in Aqueous Solution*
C. Creutz, H. A. Schwarz, J. F. Wishart, E. Fujita and N. Sutin *J. Am. Chem. Soc.* **113**, 3361-3371 (1991)
- High Pressure Pulse Radiolysis. Modification of an Optical Cell for 2-MeV Electron Pulse Radiolysis at Pressures up to 200 MPa*
J. F. Wishart and R. van Eldik *Rev. Sci. Instrum.* **63**, 3224-3225 (1992)

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High-Pressure Pulse Radiolysis Study of Intramolecular and Intermolecular Reduction of Cytochrome c by Ruthenium(II) Ammine Complexes

J. F. Wishart, R. van Eldik, J. Sun, C. Su and S. S. Isied *Inorg. Chem.* **31**, 3986-3989 (1992)

*Molecular and Electronic Structure of the Electron-Transfer Probe Analogue
[trans-(NH₃)₄Ru(imidazole)(isonicotinamide)](CF₃CO₂)₃·2-propanol*

J. F. Wishart, X. Zhang, S. S. Isied, J. A. Potenza and H. J. Schugar *Inorg. Chem.* **31**, 3179-3181 (1992)

Peptide-Mediated Intramolecular Electron Transfer: Long-Range Distance Dependence

S. S. Isied, M. Y. Ogawa and J. F. Wishart *Chem. Rev.* **92**, 381-394 (1992)

Distance Dependence of Intramolecular Electron Transfer Scross Oligoprolines in

*[*bpy*)₂Ru^{II}L[•]-(Pro)_n-Co^{III}(NH₃)₅]³⁺, n = 1-6: Effect of the Helical Polyproline II Structure*

M. Y. Ogawa, J. F. Wishart, Z. Young, J. R. Miller and S. S. Isied *J. Phys. Chem.* **97**, 11456-11463 (1993)

Long Range Electron Transfer in Helical Polyproline II Oligopeptides

M. Y. Ogawa, I. Moreira, J. F. Wishart and S. S. Isied *Chem. Phys.* **176**, 589-600 (1993)

Rate of Intramolecular Reduction of Oxyferryl Iron in Horse Heart Myoglobin

C. Fenwick, S. Marmor, K. Govindaraju, A. M. English, J. F. Wishart and J. Sun

J. Am. Chem. Soc. **116**, 3169-3170 (1994)

Mechanistic Information from the First Volume Profile Analysis for a Reversible Intermolecular Electron-Transfer Involving Isonicotinamide(pentaammine)ruthenium and Cytochrome c

B. Bänsch, M. Meier, P. Martinez, R. vanEldik, C. Su, J. Sun, S. S. Isied and J. F. Wishart
Inorg. Chem. **33**, 4744-4749 (1994)

Electron Transfer from the Heme of Cytochrome c to Two Equidistant Redox-Modified Sites, Histidine 33 and Methionine 65: The Importance of Electronic Effects and Peptide Networks

I. Moreira, J. Sun, M. O.-K. Cho, J. F. Wishart and S. S. Isied *J. Am. Chem. Soc.* **116**, 8396-8397 (1994)

Pressure Tuning Voltammetry. Reaction Volumes for Electron Transfer in Cytochrome c and Ruthenium-Modified Cytochromes c

J. Sun, J. F. Wishart, R. van Eldik, R. D. Shalders and T. W. Swaddle *J. Am. Chem. Soc.* **117**, 2600-2605 (1995)

Substituted Tetraammine Ruthenium Cytochrome c Derivatives: Chemistry and Electron Transfer Reactions

J. Sun, J. F. Wishart, M. B. Gardineer, M. P. Cho, and S. S. Isied *Inorg. Chem.* **34**, 3301-3309 (1995)

Up-Hill Electron Transfer in Pentaammineruthenium(III)-Modified Ferrocyanochrome c: Rates, Thermodynamics, and the Mediating Role of the Ruthenium Moiety

J. Sun, J. F. Wishart and S.S. Isied *Inorg. Chem.* **34**, 3998-4000 (1995)

Comparative Kinetic Analysis of Reversible Intermolecular Electron-Transfer Reactions Between a Series of Pentaammine-Ruthenium Complexes and Cytochrome c

M. Meier, J. Sun, J. F. Wishart and R. van Eldik *Inorg. Chem.* **35**, 1564-1570 (1996)

Intramolecular Electron Transfer in Pentaammineruthenium(III)-Modified Cobaltocyanochrome c

J. Sun, C. Su, and J. F. Wishart *Inorg. Chem.* **35**, 5893-5901 (1996)

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cis-Bis(bipyridine)ruthenium Imidazole Derivatives: A Spectroscopic, Kinetic, and Structural Study
K. B. Reddy, M. P. Cho, J. F. Wishart, T. J. Emge, and S. S. Isied *Inorg. Chem.* **35**, 7241-7245 (1996)

Conformational Dependence of Electron Transfer Across de novo Designed Metalloproteins
M. W. Mutz, G. McLendon, J. F. Wishart, E. R. Gaillard and A. F. Corin
Proc. Nat. Acad. Sci. **93**, 9521-9526 (1996)

Dependence of Intramolecular Electron Transfer Rates on Driving Force, pH, and Temperature in Ammineruthenium-Modified Ferrocytocochromes c
J. F. Wishart, J. Sun, M. Cho, C. Su and S. S. Isied *J. Phys. Chem. B* **101**, 687-693 (1997)

pH and Driving Force Dependence of Intramolecular Oxyferryl Heme Reduction in Myoglobin
C. W. Fenwick, A. M. English and J. F. Wishart *J. Am. Chem. Soc.* **119**, 4758-4764 (1997)

Copper(III) Pyrophosphate Complexes in Aqueous Solution. A Pulse Radiolysis Study at Ambient and High Pressure
D. E. Cabelli, J. F. Wishart, J. Holcman, M. Meier and R. van Eldik *J. Phys. Chem. A* **101**, 5131-5136 (1997)

Intramolecular Electron Transfer in Tetraammineruthenium(III)L-Modified Manganocytochromes c
J. Sun and J. F. Wishart *Inorg. Chem.* **37**, 1124-1126 (1998)

Photochemistry and Radiation Chemistry: A Perspective
J. F. Wishart in "Photochemistry and Radiation Chemistry: Complementary Methods for the Study of Electron Transfer" Wishart, J. F. and Nocera, D. G., Eds.; *Adv. Chem Ser.* **254**, Ch. 1, American Chemical Society, Washington, DC, (1998)

Accelerators and Other Sources for the Study of Radiation Chemistry
J. F. Wishart in "Photochemistry and Radiation Chemistry: Complementary Methods for the Study of Electron Transfer" Wishart, J. F. and Nocera, D. G., Eds.; *Adv. Chem Ser.* **254**, Ch. 3, American Chemical Society, Washington, DC, (1998)

Study of Oxyferryl Heme Reactivity using both Radiation and Photochemical Techniques
A. M. English, T. Fox, G. Tsaprailis, C. W. Fenwick, J. F. Wishart, J. T. Hazzard and G. Tollin in "Photochemistry and Radiation Chemistry: Complementary Methods for the Study of Electron Transfer" Wishart, J. F. and Nocera, D. G., Eds.; *Adv. Chem Ser.* **254**, Ch. 6, American Chemical Society, Washington, DC, (1998)

Electron Transfer of Bifunctional Redox Protein Maquettes
M. W. Mutz, J. F. Wishart and G. L. McLendon in "Photochemistry and Radiation Chemistry: Complementary Methods for the Study of Electron Transfer" Wishart, J. F. and Nocera, D. G., Eds.; *Adv. Chem Ser.* **254**, Ch. 10, American Chemical Society, Washington, DC, (1998)

Pulse Radiolysis Studies of Melatonin and Chloromelatonin:
J. E. Roberts, D.-N. Hu, and J. F. Wishart *J. Photochem. Photobiol. B: Biology* **42**, 125-132 (1998)

Mechanistic Information from the First Volume Profile Analysis for Intramolecular Electron-Transfer Reactions: Tetraammine-ruthenium(ligand) Complexes of Cytochrome c
J. Sun, C. Su, M. Meier, S. S. Isied, J. F. Wishart, and R. van Eldik *Inorg. Chem.* **37**, 6129-6135 (1998)

Thermodynamic and Structural Effects of a Single Backbone Hydrogen Bond Deletion in a Metal-Assembled Helical Bundle Protein
J. Zhou, M. A. Case, J. F. Wishart and G. L. McLendon *J. Phys. Chem. B* **102**, 9975-9980 (1998)

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Site-Dependent Stereoselective Binding of Ruthenium Aquobipyridine Complexes to Histidine Side Chains in Horse Heart Cytochrome c

J. Luo, J. F. Wishart and S. S. Isied *J. Am. Chem. Soc.* **120**, 12970-12971 (1998)

High Enantioselectivity in the Electron Transfer Reaction between a Ru(II) Complex of Menbpy Anion Radical, [Ru(menbpy)₃]²⁺ [menbpy=4,4'-di{(1R,2S,5R)-(-)-menthoxy carbonyl}-2,2'-bipyridine] and [Co(acac)₃]: A Pulse Radiolysis Study

T. Hamada, S. Sakaki, B. S. Brunschwig, E. Fujita and J. F. Wishart *Chem. Lett.* **1998**, 1259-1260 (1998)

The Brookhaven Laser-Electron Accelerator Facility (LEAF)

J. F. Wishart *Houshasenkagaku (Biannual Journal of the Japanese Society of Radiation Chemistry)* **66**, 63-64 (1998)

De Novo Design of Protein Function: Predictable Structure-Function Relationships in Synthetic Redox Proteins

M. W. Mutz, M. A. Case, J. F. Wishart, M. R. Ghadiri and G. L. McLendon

J. Am. Chem. Soc. **121**, 858-859 (1999)

Enantioselectivities in Electron-Transfer and Excited State Quenching Reactions of a Chiral Ruthenium Complex Possessing a Helical Structure

T. Hamada, B. S. Brunschwig, K. Eifuku, E. Fujita, M. Körner, S. Sakaki, R. van Eldik and J. F. Wishart
J. Phys. Chem. A **103**, 5645-5654 (1999)

Ruthenium Bisbipyridine Complexes of Horse Heart Cytochrome c: Characterization and Comparative Intramolecular Electron Transfer Rates Determined by Pulse Radiolysis and Flash Photolysis

J. Luo, K. B. Reddy, A. S. Salameh, J. F. Wishart and S. S. Isied *Inorg. Chem.* **39**, 2321-2329 (2000)

Design and Characterization of a Synthetic Electron-Transfer Protein

A. Y. Kornilova, J. F. Wishart, W. Xiao, R. C. Lasey, A. Fedorova, Y.-K. Shin, and M. Y. Ogawa
J. Am. Chem. Soc. **122**, 7999-8006 (2000)

Photochemical Studies on Xanthurenic Acid

J. E. Roberts, J. F. Wishart, L. Martinez, C. F. Chignell *Photochem. Photobiol.* **72**, 467-471 (2000)

Accelerators for Ultrafast Phenomena

J. F. Wishart, in "Radiation Chemistry: Present Status and Future Trends" C. D. Jonah, B. S. M. Rao, Eds.; *Studies in Physical and Theoretical Chemistry*, Vol. 87, Ch. 2, Elsevier Science, (2001), pp. 21 - 35.

Efficient Generation of the Ligand Field Excited State of Tris-(2,2'-bipyridine)-ruthenium(II) through Sequential Two-Photon Capture by [Ru(bpy)₃]²⁺ or Electron Capture by [Ru(bpy)₃]³⁺

D. W. Thompson, J. F. Wishart, B. S. Brunschwig and N. Sutin *J. Phys. Chem. A* **105**, 8117-8122 (2001)

Effect of Surface Charges on the Rates of Intermolecular Electron-Transfer between de Novo Designed Metalloproteins

A. Y. Kornilova, J. F. Wishart, and M. Y. Ogawa *Biochem.* **40**, 12186-12192 (2001)

Pulse Radiolysis Studies of Dendritic Macromolecules with Biphenyl Peripheral Groups and a Ruthenium Tris-bipyridine Core

T. H. Ghaddar, J. F. Wishart, J. P. Kirby, J. K. Whitesell, and M. A. Fox
J. Am. Chem. Soc. **123**, 12832-12836 (2001)

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Mechanistic Information from Pressure Acceleration of Hydride Formation via Proton Binding to a Cobalt(I) Macrocycle

E. Fujita, J. F. Wishart and R. van Eldik *Inorg. Chem.* **41**, 1579-1583 (2002)

A Dendrimer-Based Electron Antenna: Paired Electron Transfer Reactions in Dendrimers with a 4,4'-bipyridine Core and Naphthalene Peripheral Groups

T. H. Ghaddar, J. F. Wishart, D. W. Thompson, J. K. Whitesell, and M. A. Fox
J. Am. Chem. Soc. **124**, 8285-8289 (2002)

Spectrum and Reactivity of the Solvated Electron in the Ionic Liquid Methyltributylammonium Bis(trifluoromethylsulfonyl)imide

J. F. Wishart and P. Neta *J. Phys. Chem. B* **107**, 7261-7267 (2003)

Reactions of Charged Species in Supercritical Xenon as Studied by Pulse Radiolysis

R. A. Holroyd, J. F. Wishart, M. Nishikawa, and K. Itoh *J. Phys. Chem. B* **107**, 7281-7287 (2003)

Do Main Chain Hydrogen Bonds Create Dominant Electron Transfer Pathways? An Investigation in Designed Proteins

Y. Zheng, M. A. Case, J. F. Wishart, and G. L. McLendon *J. Phys. Chem. B* **107**, 7288-7292 (2003)

Radiation Chemistry of Ionic Liquids: Reactivity of Primary Species

J. F. Wishart in "Ionic Liquids as Green Solvents: Progress and Prospects" Rogers, R. D. and Seddon, K. R., Eds.; ACS Symp. Ser. **856**, Ch. 31, pp. 381-395, American Chemical Society, Washington, DC, 2003.

Pulse Radiolysis Study of the Reactions of Hydrogen Atoms in the Ionic Liquid Methyltributylammonium Bis(trifluoromethylsulfonyl)imide

J. Grodkowski, P. Neta and J. F. Wishart *J. Phys. Chem. A*, **107**, 9794-9799 (2003).

Radiolysis with RF Photoinjectors: Supercritical Xenon Chemistry

J. F. Wishart in "Femtosecond Beam Science" Uesaka, M., Ed.; Imperial College Press, London, in press.

Effects of Functional Group Substitution on Electron Spectra and Solvation Dynamics in a Family of Ionic Liquids

J. F. Wishart, S. I. Lall-Ramnarine, R. Raju, A. Scumpia, S. Bellevue, R. Ragbir, R. Engel *Radiat. Phys. Chem.*, in press.